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(54) **Title:** SYSTEM AND METHOD FOR CALIBRATING A SENSOR FOR MEASURING A GAS DISSOLVED IN A LIQUID

(57) **Abstract:** A system and method for determining the amount of one or more gases dissolved in a liquid, such as process water, are described, where the system comprises means for continuously supplying said liquid to an equilibrator arranged to establish equilibrium between gases in a gas phase and liquid phase, and where a sensor device measures the amount of said gas(es) in the gas phase, where the system and method comprise a calibration loop for calibrating the sensor.

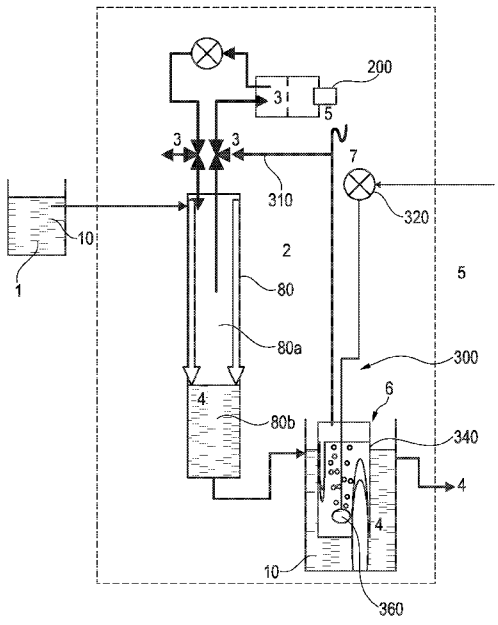


Fig. 5

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Title: **SYSTEM AND METHOD FOR CALIBRATING A SENSOR FOR MEASURING A GAS DISSOLVED IN A LIQUID**

Field of the Invention

The present invention relates to a method and system for calibrating a sensor that measures the amount of a gas dissolved in a liquid.

Background of the Invention

Fish farming has become a major industry, and in some fish farms, the formation of hydrogen sulfide and ammonia in the water where the fish are raised has led to significant problems. Hydrogen sulfide and ammonia are toxic to fish at very low concentrations, and therefore pose a challenge in the farming of marine species in closed systems. This has particularly proven to be a problem in so-called RAS systems where most of the water is recirculated back to where the fish are raised.

It has been found that hydrogen sulfide forms when there is sludge in the systems, as this creates areas with low oxygen conditions. Sulfate-reducing bacteria then convert sulfate to hydrogen sulfide. Seawater contains much larger amounts of sulfate than freshwater, and the problem of hydrogen sulfide formation is therefore greater in fish farms with seawater. Hydrogen sulfide is soluble in water, and a certain amount of hydrogen sulfide gas will be dissolved in the water where the fish are located.

Currently, there are no good practical measurement methods for measuring low concentrations of hydrogen sulfide in a liquid. It is also aimed to be able to measure other gases dissolved in liquid, such as NH_3.

In fish farms for marine organisms, such as fish, ammonia (NH_3) will be generated from feces and the fish's exhalation. Concentrations of ammonia in such fish farming liquid typically range from 1-30 ppb (parts per billion). The ammonia formed in the fish farming liquid is toxic to the fish and must be removed from the water. It is especially important to remove dissolved ammonia from the water in fish farms where the water is recirculated back to the system, i.e., in so-called RAS systems. The removal of dissolved ammonia from the water takes place in the system's biofilters, where ammonia ($NH_3(aq)$) is converted to nitrite ($NO_2(aq)$) and nitrate ($NO_3(aq)$). The concentration of NH_3 in the liquid is so low that it is practically impossible to measure the concentration.

The present invention is an improvement of existing measurement methods for measuring gas dissolved in liquid at very low concentrations. The invention builds on systems and methods previously patented by the holder Searas AS, such as the solutions described in PCT applications PCT/NO2020/050280 and PCT/NO2022/000002, and the present invention provides an improvement of these solutions. An improved calibration is introduced by changing the temperature, humidity, and pressure of the calibration gas supplied to the sensor so that it has approximately the same properties (temperature and humidity) as the liquid in which the gas measurement is to be performed.

Description of Prior Art

There are currently sensors for measuring H_2S in freshwater. These are used, for example, for drinking water analysis. In seawater, the need to measure H_2S has only recently arisen, especially in RAS systems for marine fish species such as salmon. H_2S is highly toxic and easily soluble in water. Seawater contains 2700 mg of sulfate per liter compared to 2.2 mg/liter for freshwater.

Sulfate-reducing bacteria are anaerobic bacteria that form H_2S. This occurs in areas of the fish tank or water treatment system where there is poor water circulation. It also occurs in the biofilter if anaerobic conditions arise. Under a heterotrophic biofilm,

there will also be anaerobic conditions. Small amounts of H_2S are produced here, and therefore there will always be a certain background level of H_2S in all RAS systems. This level is low, often around 100 ng/liter, and is therefore difficult to measure in water. The sensors are also very susceptible to the corrosive seawater environment.

There are currently methods for measuring H_2S in the range of 1000-50000 ng/liter. This instrumentation is very expensive, and it is of interest to find solutions to monitor H_2S concentrations below 1000 ng/liter to get an early warning that things are starting to happen in the fish farm. To measure at such low concentrations, it is very important to have an accurate method for calibrating the sensors. This also applies to NH3. As explained, NH_3 accumulates in the water. It is kept in check in RAS systems by biofilters converting ammonia to nitrite and then to nitrate. In flow-through systems where there are no biofilters, ammonia will accumulate, and the way to control it is by changing the water. It is therefore very important to be able to monitor these levels in real-time and have a good method for calibrating the sensors so that accurate values can be recorded at these very low levels.

Summary of the Invention

The present invention relates in a first aspect to a system for determining the amount of one or more gases dissolved in a liquid, such as process water, where the system comprises means for continuously supplying said liquid to an equilibrator arranged to establish equilibrium between gases in a gas phase and a liquid phase, and where a sensor device measures the amount of said gas(es) in the gas phase, characterized in that the system comprises a calibration loop where a calibration gas is introduced to the sensor device and where the system comprises means arranged to change the properties of said calibration gas such as humidity, temperature, or pressure before the calibration gas is introduced into the sensor device. Preferably, said means is a closed container arranged surrounded by liquid in a tank.

In one embodiment, the properties of the calibration gas such as humidity, temperature, or pressure are changed to the same or approximately the same values as the gas in the gas phase.

In one embodiment, gases from the gas phase in a closed gas volume are brought into contact with the liquid phase.

In one embodiment, the system comprises an air pump arranged to pump calibration gas through the system to the sensor device.

In one embodiment, the system comprises means arranged to change the temperature and humidity of the calibration gas.

In one embodiment, said means is a closed container arranged surrounded by liquid in a tank.

In one embodiment, calibration gas is supplied through a diffuser stone arranged to form small bubbles.

In one embodiment, the system comprises a gas transporter arranged to cause circulation of gases from the gas phase to the liquid phase.

In one embodiment, the equilibrator has an outlet with a water lock to regulate the liquid level in the equilibrator.

In one embodiment, the sensor device measures the amount of gases directly in the gas phase in the equilibrator.

In one embodiment, gases from the gas phase are circulated in a closed loop through the liquid phase.

In one embodiment, the system comprises a gas transporter that transports gases in a closed loop from the gas phase to the liquid phase.

In one embodiment, the gas transporter comprises a pump and a pipeline for transporting gases from the gas phase to the liquid phase.

In one embodiment, the system comprises a closed loop and that gases from the gas phase are transported by a gas transporter to the liquid phase via this loop, and that a sensor device is arranged in the loop and measures the amount of one or more gases in the gas phase.

In one embodiment, gas from the gas phase is circulated in a closed loop via a sensor device for measuring the amount of a given gas.

In one embodiment, the gas supply unit is a hose equipped with an air pump to draw gas from the gas phase and supply it to the liquid phase.

In one embodiment, the gas transporter is an ejector.

In one embodiment, liquid is supplied via pump and pipelines to the top of the equilibrator and the ejector arranged in the liquid phase in the equilibrator, and that gases from the gas phase are drawn into the ejector via pipeline.

In one embodiment, a foam suppressor is arranged in the gas phase in the equilibrator.

In one embodiment, the foam suppressor is arranged in the equilibrator so that there is a gas phase above the foam suppressor.

In one embodiment, gases are drawn to the sensor device from the gas phase below the foam suppressor and that gases returning from the sensor device return to the equilibrator via the gas phase above the foam suppressor.

In one embodiment, liquid is supplied to the equilibrator via a nozzle, arranged to spread the water over the cross-section of the equilibrator or that the liquid is supplied and flows down along the inner surfaces of the equilibrator.

In one embodiment, the gas transporter is a diffuser.

In one embodiment, gases from the gas phase are pumped from the foam suppressor to the diffuser.

In one embodiment, the equilibrator is arranged substantially horizontally and that gases are circulated in a closed loop through the gas phase in the equilibrator using a pump or propeller.

In one embodiment, the sensor device is connected to the closed loop.

In one embodiment, liquid is transferred to the equilibrator via nozzles, and supplied to the end edge of the equilibrator where it flows out through a pipeline with a water lock.

In one embodiment, the measurements of the amount of gas are calibrated with measurements of a gas mixture, such as air, with a known gas composition.

In one embodiment, the calibration takes place in a closed loop equipped with valves, and that the calibration is performed automatically at given times.

In one embodiment, liquid supplied to the equilibrator is drawn from a first container.

In one embodiment, the system comprises a container upstream of the equilibrator and downstream of the container for regulating the pH of the liquid before it is transferred to the equilibrator.

In one embodiment, the container arranged to regulate the pH of the liquid comprises means for adding a pH-regulating agent to the container.

In one embodiment, the pH-regulating agent can be in the form of a gas, a liquid, or a solid.

In a second aspect, the present invention relates to a method for determining the amount of a gas dissolved in a liquid, characterized by continuously supplying the liquid in a closed loop to an equilibrator arranged to establish equilibrium between the gases in a gas phase and the gases dissolved in a liquid phase in the equilibrator, and where gases from the gas phase in a closed gas volume are brought into contact with the liquid phase, and a sensor device measures the amount of one or more gases in the gas phase, characterized by introducing a calibration gas to the sensor device and where the system comprises means arranged to change the properties of said calibration gas such as humidity, temperature, or pressure before the calibration gas is introduced into the sensor device.

In one embodiment, the properties of the calibration gas such as humidity, temperature, or pressure are changed to the same or approximately the same values as the gas in the gas phase.

In one embodiment, gases from the gas phase, in a closed gas volume, are brought into contact with the liquid phase.

In one embodiment, an air pump pumps calibration gas through the system to the sensor device.

In one embodiment, the temperature and humidity of the calibration gas are changed before it is introduced to the sensor.

In one embodiment, calibration gas is supplied through a diffuser stone arranged to form small bubbles.

In one embodiment, a gas transporter causes circulation of gases from the gas phase to the liquid phase.

In one embodiment, gases from the gas phase are transported by a gas transporter to the liquid phase in a closed loop, and a sensor device is arranged in the loop and measures the amount of one or more gases in the gas phase.

In one embodiment, gas from the gas phase is circulated in a closed loop via a sensor device for measuring the amount of a given gas.

In one embodiment, the sensor device measures the amount of one or more gases selected from hydrogen sulfide, carbon dioxide, oxygen, and ammonia.

In one embodiment, the gas is hydrogen sulfide.

In one embodiment, the flow rate and amount of liquid through the equilibrator are measured or calculated, so that the absolute amount of gas dissolved in the liquid can be calculated.

In one embodiment, the gas transporter generates microbubbles in the liquid phase.

In one embodiment, the liquid is continuously transferred from a first container to the equilibrator.

In one embodiment, a system according to any of claims 1-33 is arranged in multiple locations in a fish farm.

In one embodiment, the system is arranged to measure gas amounts in liquid entering the fish tank.

In one embodiment, the system is arranged to measure gas amounts released from the system via the CO2 stripper.

In one embodiment, the liquid is supplied with a pH-regulating agent after leaving the container and before being transferred to the equilibrator, to adjust the pH of the liquid so that the equilibrium between the gas dissolved in the liquid and its ions dissolved in the liquid shifts, resulting in more gas being dissolved in the liquid.

In one embodiment, the change in pH due to the addition of the pH-regulating agent is used to calculate the amount of gas dissolved in the liquid in the container based on measurements of the amount of said gas in the gas phase corrected for the change in the amount of gas due to the change in pH.

Description of Figures

Preferred embodiments of the invention will be described in more detail below with reference to the accompanying figures, where:

Figure 1 schematically shows a system for measuring the concentration or amount of a gas in a liquid. The liquid is transferred in a continuous flow to an equilibrator, and the amount of gas is measured in the gas phase in this equilibrator.

Figure 2 shows the same solution as Figure 1, but additionally includes a gas transporter for transporting gases from the gas phase in the equilibrator to the liquid phase in the equilibrator.

Figure 3 schematically shows a system for measuring the amount of a gas dissolved in a liquid. The liquid is transferred in a continuous flow to an equilibrator via a container for adjusting the liquid's pH.

Figure 4 shows the same solution as in Figure 1, but additionally includes a gas transporter for transporting gases from the gas phase in the equilibrator to the liquid phase in the equilibrator.

Figure 5 shows an embodiment according to the invention where a calibration loop is introduced to ensure that the calibration gas is given the same temperature and humidity as the process liquid.

Description of Preferred Embodiments of the Invention

Methods and systems for measuring the amount of a gas dissolved in a liquid are described in PCT applications PCT/NO2020/050280 and PCT/NO2022/000002.

The liquid (for example, water in a fish farm) is transferred to an equilibrator in a continuous flow. The equilibrator is a container where equilibrium is established between gases in the liquid phase 80b and in the gas phase 80a. Optionally, gases from the gas phase 80a are brought into contact with the liquid phase to achieve an efficient exchange of gases between the gas and liquid phases, so that equilibrium between gases in the gas phase and liquid phase is established more quickly.

In one embodiment, this is achieved by circulating the gases passing through the sensor box in a closed loop through the water flowing through the equilibrator. This will establish an equilibrium between the water and the gas above the water surface, so that the gases in this gas phase at all times reflect the content of gases in the liquid phase.

The sensors therefore measure gases that are in equilibrium with the liquid and are not directly exposed to the liquid, avoiding problems such as fouling, maintenance, sensor lifespan, and accuracy.

Figure 1 schematically shows a general embodiment for measuring gases dissolved in a liquid 10, where the concentration or amount of a given gas dissolved in a liquid 10 in a container 11 is to be measured. The container 11 can, for example, be a closed fish farming pen or the tank in a RAS system.

Since there are no sensors that can measure low H2S concentrations in the liquid 10, especially when this liquid 10 is seawater, the liquid 10 is transferred in a continuous

flow using a pump 62 via a pipeline 60 to an equilibrator 80. In Figure 1, it is shown that the liquid is supplied to the upper part of the equilibrator, but the liquid 10 can, in principle, be supplied to any part of the equilibrator 80, including the liquid phase 80b at the bottom of the equilibrator 80. Preferably, the liquid is supplied so that it flows down along the inner sides of the equilibrator 80.

From the equilibrator 80, an outlet 70 is arranged to regulate the water level in the equilibrator 80.

In the equilibrator 80, an equilibrium is established with respect to the amount of gases between the liquid phase 80b and the gas or air phase 80a, so that the amount of a given gas in the gas phase 80a is correlated to the amount of this gas in the liquid phase 80b. Since the liquid 10 continuously flows from the container 11 to the equilibrator 80, and since the system is closed, the content of a given gas in the gas phase 80a is correlated to the amount of this gas dissolved in the liquid 10 in the container 11. The actual gas content in the liquid 10 in the container 11 can then be calculated based on the measurement of the gas content in 80a.

This solution represents a completely new principle for measuring the amount or concentration of a gas in a liquid, by having the liquid flow through the equilibrator. Gases from the gas phase 80a are circulated in a closed loop that is in contact with or flows through the liquid phase 80b, establishing an equilibrium between gases in the liquid phase 80b and the gas phase 80a. The gas measurement is performed in the gas phase 80a, but reflects the amounts of gas in the liquid phase 80b. This avoids the sensors being in contact with the liquid 10. This principle can be used for measuring any gas, but is particularly suitable for monitoring gases that are difficult to measure directly in the liquid.

The system and method according to the invention are specifically developed to measure low concentrations of H_2S and NH_3, but can also be used for other gases and also when the amounts of gas dissolved in the liquid are larger.

In the simplest embodiment of the invention, the sensors 200 are placed directly in the gas phase 80a. This solution is not shown in the figures. If the liquid is trickled/sprayed into the equilibrator 80, no additional means are needed to transport gas from the gas phase 80a to the liquid phase 80b. However, it is often preferable to have other means arranged in the equilibrator 80 to transfer gases from the gas phase 80a to 80b.

Figure 1 shows a more preferred solution for measuring the concentration and amount of gases. A pipeline 200a carries the gases using a pump 202 from the gas phase 80a via a sensor device 200, and back to the equilibrator 80, preferably via the liquid phase 80b in the equilibrator 80. This circuit is closed, and no gases or air are supplied from outside as the gases only circulate from the gas phase 80a to the liquid phase 80b, via the sensor device 200. This circulation of gases is beneficial for establishing equilibrium between gases in the liquid phase 80b and the gas phase 80a, and the measurements of a given gas are most accurate when there is near equilibrium in the equilibrator 80.

It is schematically indicated in the sensor device 200 that it comprises sensors S1, S2, and S3, which can, for example, be sensors for measuring H2S, CO2, and O2, which are important gases to monitor in a RAS system.

Figure 2 shows essentially the same solution as in Figure 1, but includes an additional gas transporter 100 to improve the exchange of gases between the gas phase 80a and the liquid phase 80b, i.e., so that equilibrium in the equilibrator 80 is established more quickly. The gas transporter 100 in Figure 2 is a pipeline extending from the gas phase 80a to the liquid phase 80b, equipped with a pump 102 so that gas can be transported from the gas phase 80a to the liquid phase 80b. The circuit is closed, and no gas is supplied to the system, only a transfer from 80a to 80b to improve the exchange of gases between the two phases.

In Figure 2, this gas transporter 100 is schematically shown arranged inside the equilibrator 80, but in an alternative embodiment, it is arranged outside the equilibrator 80 with pipelines extending through the equilibrator 80 so that gases can be transferred from 80a to 80b.

Experiments have shown that it is beneficial for the gases released from the gas transporter into the liquid phase 80b to be in the form of small air bubbles, preferably microbubbles. These have a large surface area relative to volume, i.e., a relatively large interface between liquid and gas, which enables efficient gas exchange between 80a and 80b, and a rapid establishment of equilibrium in the equilibrator 80.

In addition to the principle of transferring the liquid to an equilibrator to measure the amount of gas dissolved in the liquid (for example, to measure the amount of H2S in a fish farm), an improved method was developed, for example, to measure NH3 by adjusting the pH of the liquid.

Figure 3 schematically shows such a system for adjusting the pH of a liquid before the gas amount in the liquid is measured in an equilibrator 80. The goal is to measure the amount or concentration of a given gas in a liquid contained in a container 11. This can, for example, be a fish farm, such as a RAS system. Conventional methods for measuring gas amounts for many types of gas are not sufficiently sensitive to measure the gas amount in the liquid in the container 11 itself. Therefore, the liquid is transferred to an equilibrator 80 via pipelines 60, using a pump 62. Associated with the equilibrator 80 is a water lock 70 at the outlet to regulate the liquid level in the equilibrator 80. After a while, an equilibrium for the gas to be measured will be established between the amount of gas dissolved in the liquid 80b in the equilibrator 80 and the amount of gas dissolved in the gas phase 80a above the liquid level in the equilibrator 80. It is preferred that this equilibrium between gas dissolved in the liquid phase 80b and the gas phase 80a is established quickly so that the measurements of the amount of the relevant gas, measured using sensors 200 in the gas phase 80a,

can be performed continuously. To facilitate a rapid establishment of this equilibrium between gas in the liquid phase 80b and the gas phase 80a, the system is preferably equipped with means to facilitate the circulation of the gas phase 80a to the liquid phase 80b. If gases from the gas phase 80a are transported to the liquid phase 80b, and preferably also transported through the liquid phase 80b, the equilibrium between gases in the liquid phase 80b and the gas phase 80a will be established more quickly. These means for transporting gases through the liquid phase 80b are schematically illustrated in some of the figures as a gas transporter with reference number 100. In a simple preferred embodiment, the gas measured in sensor 200 is transported to a lower level in the liquid phase 80b so that bubbles of gas phase 80a rise through the liquid phase 80b.

It is not necessary for the gases from the gas phase 80a to be used to transport gases through the liquid phase 80b. Any gas passed through the liquid phase 80b will facilitate a faster establishment of equilibrium between gas in the gas phase 80a and the liquid phase 80b. Thus, it is often preferred to bubble another gas, such as air or oxygen, through the liquid phase 80b to facilitate this faster establishment of equilibrium. For example, air or oxygen can be supplied using an injector or ejector directly to the liquid phase 80b. It is preferred that the gas (e.g., air) supplied to the liquid phase 80b forms small bubbles, preferably microbubbles, in the liquid phase 80b. Such bubbles, and preferably microbubbles, establish a relatively large interface between gases in the gas phase 80a (which also includes the volume inside the bubbles) and gases in the liquid phase 80b. A larger interface accelerates the establishment of equilibrium.

The supply of gas or gases to the liquid phase 80b can be done in many different ways, and the gas transporters can thus vary. Figure 4 schematically shows this gas transporter 100 arranged inside the equilibrator 80, but in an alternative embodiment, it is arranged outside the equilibrator 80 with pipelines extending through the equilibrator 80 so that gases can be transferred from 80a to 80b, i.e., gases are extracted from the gas phase 80a and supplied, preferably at a lower level, to the liquid phase 80b. Experiments have shown that it is beneficial for the gases released

from the gas transporter into the liquid phase 80b to be in the form of small air bubbles, preferably microbubbles. As mentioned above, microbubbles have a large surface area relative to volume, i.e., a relatively large interface between liquid and gas, which enables efficient gas exchange between 80a and 80b, and a rapid establishment of equilibrium in the equilibrator 80.

In an embodiment as described above, sensors 300a are arranged to measure the pH in the fish tank 11 itself, so that the pH can be measured at any time before adding the pH-regulating agent. Furthermore, the pH can be measured using sensor 300b to measure the pH in the liquid phase 80b of the solution in the equilibrator 80. The sensor 300b for measuring the pH after adding the pH-adjusting agent can also be arranged in the pipeline that leads the liquid 10 from the container 20 for pH adjustment to the equilibrator 80. Conventional pH meters can be used, and preferably these are read automatically, and the results are sent to a control unit so that the pH of the solution before adding the pH-regulating agent and the pH after adding it can be continuously monitored. Based on this pH change, and the mentioned tables and graphs, the number of times the concentration of NH3 has changed after adding the pH-regulating agent can be calculated, and it can be corrected back to calculate how much NH3 was originally present in the liquid 10, i.e., before adding the pH-regulating agent. By adjusting the pH before measuring NH3, the sensitivity of the measurement is increased as the equilibrium between gas dissolved in the liquid and its corresponding ions dissolved in the liquid is shifted to a pH value where the equilibrium is shifted towards the gas. For the NH3 system, this means that if the pH of the liquid is increased, the amount of NH3 (aq) in the liquid 10 increases.

Alternatively, instead of measuring the pH both before and after adding the pH-regulating agent, the pH-regulating agent can be dosed in such a way that the amount added is fully controlled. When the amount of pH-regulating agent added is known, and also the effect this addition has on the equilibria in the liquid 10, the pH value after addition can be calculated, and this calculated value can be used to determine the number of times the amount of the relevant gas, such as NH3, has

increased with the pH adjustment. Figure 7 schematically shows a system where a container 350 for receiving the pH-regulating agent is arranged. The pipeline leading from the container 350 to the container 20 is equipped with a dosing unit 400 that controls and measures the amount of pH-regulating agent added. If the pH-regulating agent is a liquid, it is preferred that the dosing unit measures the amount in volume added, for example, the number of milliliters of pH-regulating liquid added. If the pH-regulating agent is a powder, the dosing unit 400 can preferably dose and measure the amount based on weight. Such dosing units 400 are conventional and can be purchased.

The system and method according to the invention are described for measuring NH3 in a fish farm, but we emphasize that other gases can also be measured, especially other gases that shift the equilibrium between gas and ions dissolved in the liquid if a pH change is imposed. We also emphasize that other gases can be measured with the system and method, i.e., without adjusting the pH, or without this affecting the amount of the mentioned gas in the liquid 10, but by simply using the effect of transferring the liquid to an equilibrator to measure the amount of gas in the gas phase 80a and not in the liquid 10 itself. We also emphasize that multiple gases can be measured simultaneously by using multiple sensors 200, each specific to at least one of the mentioned gases to be measured. The invention provides an opportunity for continuous measurement of gases in liquids in a facility, such as a fish farm. Individually, and in combination, the two principles; (i) measuring gas levels in the gas phase when the liquid is in an equilibrator 80 and equilibrium is established between the mentioned gas in the gas phase 80a and the liquid phase 80b, and (ii) adjusting the pH of the liquid 10 to shift the equilibrium towards more dissolved gas in the liquid to indirectly measure smaller amounts of gas in the liquid, bring new opportunities for continuous control of gas concentrations in the liquid, especially gases that can have a harmful effect on species, such as fish, that are farmed in the liquid 10 in the container 11. The method and system provide an opportunity for continuous control over the development of gases in the liquid. Relative values can be easily measured, i.e., changes in the amount of a given gas can be measured,

but one can also easily calculate the absolute values and determine if these are approaching a level that would be harmful to the fish, so that measures can be taken.

Figure 5 schematically describes the present invention, i.e., a method and system for calibrating a sensor used for measuring one or more gases dissolved in a liquid. The system and method shown in Figure 5 are an improvement over existing methods as they allow the sensor to be calibrated with a gas that has the same temperature, humidity, and pressure as the process liquid 10.

It has been found that several types of sensors that measure gases in the air are often affected not only by the gas they are supposed to measure but also by factors such as pressure, humidity, and temperature, and to some extent, other gases. This is because a sensor often bases its measurement principle on the current passing through the sensor element itself. A sensor affected by dry air may conduct current less effectively than a sensor surrounded by air with high humidity.

When specifying a measurement range for a sensor, factors other than the gas the sensor is supposed to measure will influence the measurement.

A sensor that measures gases in the air is often calibrated against air with known gas content or partial pressure. For example, we know that gases in the atmosphere have known contents such as CO_2 - 420 ppm, O_2 - 20.95%, H_2S - 0 ppm, NH_3 - 0 ppm. When calibrating a sensor against one of the aforementioned gases, it will be calibrated against the content of the relevant gas, but also in most uses of a sensor, the pressure, temperature, and RH will be the same as in the air being measured.

We have developed a system for measuring gases in water, especially in aquaculture. Here, the water often has a temperature adapted to the fish. There is often a need to measure very low values of gases dissolved in water because fish have very low tolerances for gases such as H_2S and NH_3.

The described method shows how sensors with a measurement range that is normally too high can be used when there is a need to measure very small concentrations. This means that the sensitivity and precision of the sensor are increased by introducing a calibration loop (as described below).

Air from outside, with a known content of gases such as CO_2 - 420 ppm, O_2 - 20.95%, H_2S - 0 ppm, NH_3 - 0 ppm, is used as the calibration gas while the humidity and temperature of the calibration gas are adjusted in the calibration loop to match those of the process water/liquid 10.

The calibration loop 300 includes a pump 320 for intake of a known gas such as air. The gas (air) taken in by the pump 320 is led into a humidifier and temperature adjuster 340, such as a closed container 340 arranged to be surrounded by process liquid 10, which will set the temperature in the container 340 to the same temperature as the process water 10. The process water is led through tank 10, which contains a closed container 340 with distilled water. The tank 10 and the closed container 340 will then achieve the same temperature as the process water. The calibration air is led into the closed container 340 and rises through the water, achieving the same temperature and approximately 100% humidity before being led to the sensor elements 200 for calibration verification. To perform an accurate calibration of especially H_2S and NH_3 gas sensors at low values, it is crucial that the calibration gas has the same temperature and humidity as the gas being measured.

For example, if the calibration air in winter has a temperature of -10 degrees, the humidity (RH) of the air reaching the sensor 200 will be drastically reduced since this air normally does not pass through the equilibrator (80). Therefore, a separate air calibration pump (320) is introduced, which draws air from, for example, the atmosphere and pumps it through a "humidifier and temperature adjuster" (LFTI) (340). The LFTI (340) contains clean water through which the gas is pumped. At the same time, the water is surrounded by process water 10, so it achieves the same

temperature as the process water 10. It is important that the temperature transfer from the process water is sufficient concerning the temperature influences from the gas being pumped through the water.

When the air is pumped down into the water in (340), it can preferably pass through a diffuser stone 360 or similar, forming small bubbles. These will more easily achieve the same temperature and humidity (RH). The gas above the liquid phase in the container 340 is then led to the sensor for calibration.

Example 1

Measurement of NH_3

Before we introduced the calibration loop, we observed that the humidity changed from 79.7% to 74.8% during the regular calibration of the sensor. This is measured by the NH3 sensor. This causes the sensor to register less NH3 gas, meaning it is not sufficiently sensitive.

After we introduced the calibration loop (as described above), the calibration air (310) had the same temperature and humidity as the process air (gas phase 80a from the equilibrator). Then the humidity in the sensor housing changed very little (80.1% to 80.3%). This means that when we calibrate, we find the zero point for NH3 (based on the fact that outdoor air does not contain NH3) with the same influence of temperature and humidity from both process air and calibration air.

We see that when water is pumped into the equilibrator, the air passing through the sensor housing is cooled, and then the RH measured will decrease.

We have conducted a calibration test with calibration loop 300. We measured a small change in humidity and had to compensate with approximately 30 ppb (parts per billion). 30 ppb is a very small difference. With such calibration, we achieve the ability to measure changes in TAN (Total Ammonium Nitrogen) of approximately 0.03 mg.

Patent Claims

1. System for determining the amount of one or more gases dissolved in a liquid (10), such as process water (10), where the system comprises means for continuously supplying said liquid (10) to an equilibrator (80) arranged to establish equilibrium between gases in a gas phase (80a) and liquid phase (80b), and where a sensor device (200) measures the amount of said gas(es) in the gas phase (80a), characterized in that the system comprises a calibration loop (300) where a calibration gas (310) is introduced to the sensor device (200) and where the system comprises means (340) arranged to change said calibration gas (310) properties such as humidity, temperature, or pressure before the calibration gas (310) is introduced into the sensor device (200), where said means (340) is a closed container (340) arranged to be surrounded by liquid (10) in a tank (350).

2. System according to claim 1, characterized in that the properties of the calibration gas (310) such as humidity, temperature, and pressure are changed to the same or nearly the same values as the gas in the gas phase (80a).

3. System according to claim 1, characterized in that gases from the gas phase (80a) in a closed gas volume are brought into contact with the liquid phase (80b).

4. System according to claim 1, characterized in that the system comprises an air pump (320) arranged to pump calibration gas (310) through the system to the sensor device (200).

5. System according to claim 1, characterized in that the system comprises means (340) arranged to change the temperature and humidity of the calibration gas (310).

6. System according to claim 1, characterized in that the calibration gas (310) is supplied through a diffuser stone (360) arranged to form small bubbles.

7. System according to claim 1, characterized in that the system comprises a gas transporter (100, 100', 100'') arranged to cause circulation of gases from the gas phase (80a) to the liquid phase (80b).

8. System according to claim 1, characterized in that the equilibrator (80) has an outlet (70) with a water lock to regulate the liquid level in the equilibrator (80).

9. System according to claim 1, characterized in that the sensor device (200) measures the amount of gases directly in the gas phase (80a) in the equilibrator (80).

10. System according to claim 1, characterized in that gases from the gas phase are circulated in a closed circuit through the liquid phase (80b).

11. System according to claim 1, characterized in that the system comprises a gas transporter (100, 100', 100'') that transports gases in a closed circuit from the gas phase (80a) to the liquid phase (80b).

12. System according to claim 1, characterized in that the gas transporter (100, 100', 100'') comprises a pump (102) and a pipeline (100) for transporting gases from the gas phase (80a) to the liquid phase (80b).

13. System according to claim 1, characterized in that the system comprises a closed loop (200a) and that gases from the gas phase (80a) are transported by a gas transporter (100) to the liquid phase (80b) via this loop (200a), and that a sensor device (200) is arranged in the loop (200a) and measures the amount of one or more gases in the gas phase (80a).

14. System according to claim 1, characterized in that gas from the gas phase (80a) is conducted in a closed circuit via a sensor device (200) for measuring the amount of a given gas.

15. System according to claim 1, characterized in that the gas supply unit (100) is a hose (100) equipped with an air pump (102) to draw gas from the gas phase (80a) and supply it to the liquid phase (80b).

16. System according to claim 4, characterized in that the gas transporter (100, 100', 100'') is an ejector (100').

17. System according to claim 10, characterized in that liquid (10) is fed via a pump (62) and pipelines (60) to the top of the equilibrator (80) and the ejector (100') arranged in the liquid phase (80b) in the equilibrator (80), and that gases from the gas phase (80a) are drawn into the ejector (100') via pipeline (100).

18. System according to claim 1, characterized in that a foam suppressor (120) is arranged in the gas phase (80a) in the equilibrator (80).

19. System according to claim 19, characterized in that the foam suppressor (120) is arranged in the equilibrator (80) so that there is a gas phase (80a) above the foam suppressor (120).

20. System according to claim 19, characterized in that gases (80a) to the sensor device (200) are drawn from the gas phase (80a) below the foam suppressor and that gases (80a) returning from the sensor device (200) return to the equilibrator (80) via the gas phase (80a) above the foam suppressor (120).

21. System according to claim 1, characterized in that the liquid (10) is supplied to the equilibrator (80) via a nozzle (130), arranged to spread the water over the cross-section of the equilibrator (80) or that the liquid (10) is supplied and flows down along the inner surfaces of the equilibrator (80).

22. System according to claim 1, characterized in that the gas transporter (100, 100', 100") is a diffuser (100").

23. System according to claim 18, characterized in that gases from the gas phase (80a) are conducted via a pump 102" from the foam suppressor to the diffuser (100").

24. System according to claim 1, characterized in that the equilibrator (80) is arranged essentially horizontally and that gases are circulated in a closed circuit through the gas phase (80a) in the equilibrator (80) using a pump or propeller.

25. System according to claim 1, characterized in that the sensor device (200) is connected to the closed circuit.

26. System according to claim 21, characterized in that the liquid (10) is transferred to the equilibrator (80) via nozzles (130'), and is transferred to the end edge of the equilibrator (80) where it flows out through pipeline (70) with a water lock.

27. System according to claim 1, characterized in that the measurements of the amount of gas are calibrated with measurements of a gas mixture, such as air, with a known gas composition.

28. System according to claim 27, characterized in that the calibration takes place in a closed circuit equipped with valves, and that the calibration is performed automatically at given times.

29. System according to claim 1, characterized in that the liquid (10) supplied to the equilibrator (80) is drawn from a first container (11).

30. System according to claim 1, characterized in that the system comprises a container (20) upstream of the equilibrator (80) and downstream of the container (11) for regulating the pH in the liquid (10) before it is transferred to the equilibrator (80).

31. System according to claim 30, characterized in that the container (20) arranged to regulate the pH in the liquid (10) comprises means (20a) for adding a pH-regulating agent to the container (20).

32. System according to claim 30, characterized in that the pH-regulating agent can be in the form of a gas, a liquid, or a solid.

33. Method for determining the amount of a gas dissolved in a liquid characterized in that the liquid (10) is continuously supplied in a closed circuit to an equilibrator (80) arranged to establish equilibrium between the gases in a gas phase (80a) and the gases dissolved in a liquid phase (80b) in the equilibrator (80), and that gases from the gas phase (80a) in a closed gas volume are brought into contact with the liquid phase (80b), and that a sensor device (200) measures the amount of one or more gases in the gas phase (80a), characterized in that a calibration gas (310) is introduced to the sensor device (200) and where the system comprises means arranged to change said calibration gas (310) properties such as humidity, temperature, or pressure before the calibration gas (310) is introduced into the sensor device (200).

34. Method according to claim 33, characterized in that the properties of the calibration gas (310) such as humidity, temperature, and pressure are changed to the same or nearly the same values as the gas in the gas phase (80a).

35. Method according to claim 33, characterized in that gases from the gas phase (80a) in a closed gas volume are brought into contact with the liquid phase (80b).

36. Method according to claim 33, characterized in that an air pump (320) pumps calibration gas (310) through the system to the sensor device (200).

37. Method according to claim 33, characterized in that the temperature and humidity of the calibration gas (310) are changed before it is introduced to the sensor (200).

38. Method according to claim 33, characterized in that the calibration gas (310) is supplied through a diffuser stone (360) arranged to form small bubbles.

39. Method according to claim 33, characterized in that a gas transporter (100, 100', 100") causes circulation of gases from the gas phase (80a) to the liquid phase (80b).

40. Method according to claim 39, characterized in that gases from the gas phase (80a) are transported by a gas transporter (100) to the liquid phase (80b) in a closed loop (200a), and that a sensor device (200) is arranged in the loop (200a) and measures the amount of one or more gases in the gas phase (80a).

41. Method according to claim 33, characterized in that gas from the gas phase (80a) is conducted in a closed circuit via a sensor device (200) for measuring the amount of a given gas.

42. Method according to claim 33, characterized in that the sensor device (200) measures the amount of one or more gases selected from hydrogen sulfide, carbon dioxide, oxygen, and ammonia.

43. Method according to claim 33, characterized in that the gas is hydrogen sulfide.

44. Method according to claim 33, characterized in that the flow rate and amount of liquid through the equilibrator are measured or calculated, so that the absolute amount of gas dissolved in the liquid (10) can be calculated.

45. Method according to claim 33, characterized in that the gas transporter (100, 100', 100") generates microbubbles in the liquid phase (80b).

46. Method according to claim 33, characterized in that the liquid (10) is continuously transferred from a first container (11) to the equilibrator (80).

47. Method according to claim 33, characterized in that a system according to any of claims 1-33 is arranged at multiple locations in an aquaculture facility.

49. Method according to claim 38, characterized in that the system is arranged to measure gas amounts in liquid entering the aquaculture tank (11').

49. Method according to claim 38, characterized in that the system is arranged to measure gas amounts exiting the facility via the CO2 stripper (16).

50. Method according to claim 33, characterized in that the liquid (10) after leaving the container (11) and before being transferred to the equilibrator (80) is supplied with a pH-regulating agent to adjust the pH in the liquid (10) so that the equilibrium between said gas dissolved in the liquid (10) and its ions dissolved in the liquid (10) shifts so that more gas is dissolved in the liquid (10).

51. Method according to claim 50, characterized in that the change in pH due to the addition of the pH-regulating agent is used to calculate the amount of gas dissolved in the liquid (10) in the container (11) based on measurements of the amount of said gas in the gas phase (80a) corrected for the change in the amount of gas due to the change in pH.

52. Method according to claim 50, characterized in that the amount of pH-regulating agent is measured, and that the amount of pH-regulating agent added is used to calculate the change in pH before and after the addition of the pH-regulating agent, and that the change in pH is used to calculate the amount of gas dissolved in the liquid (10) in the container (11) based on measurements of the amount of said gas in the gas phase (80a) corrected for the change in the amount of gas due to the change in pH.

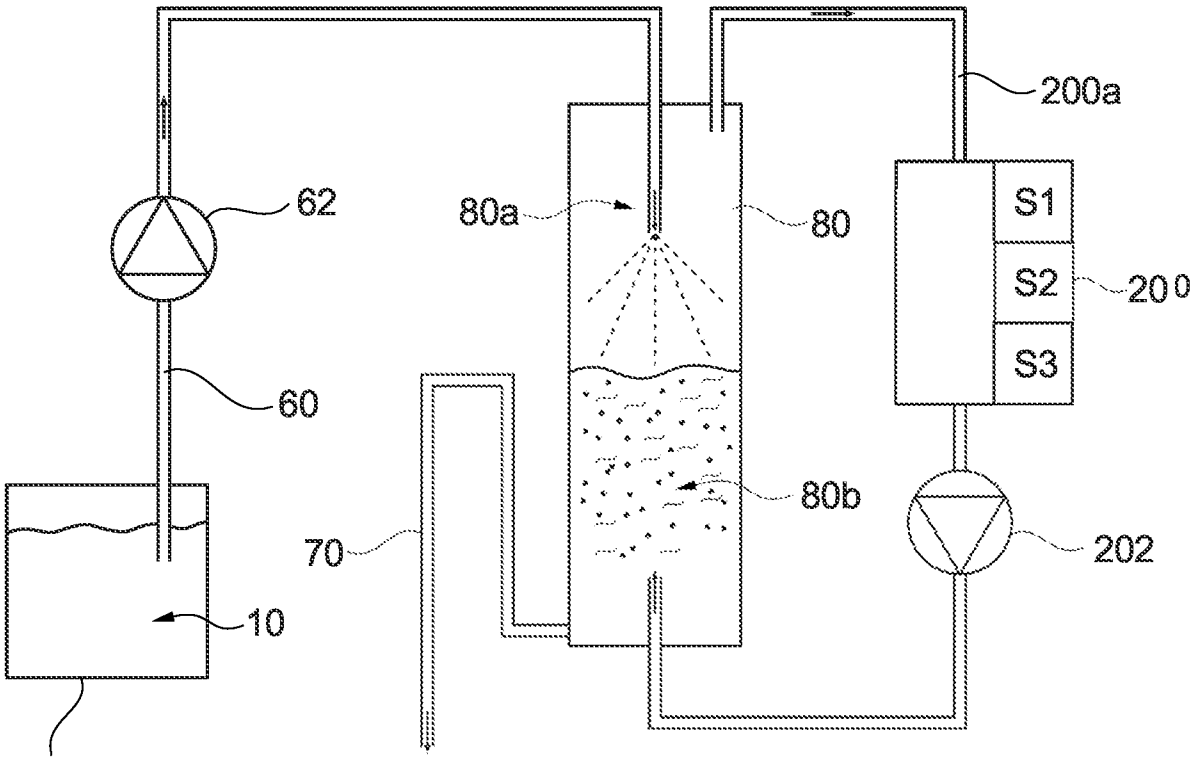


Fig. 1

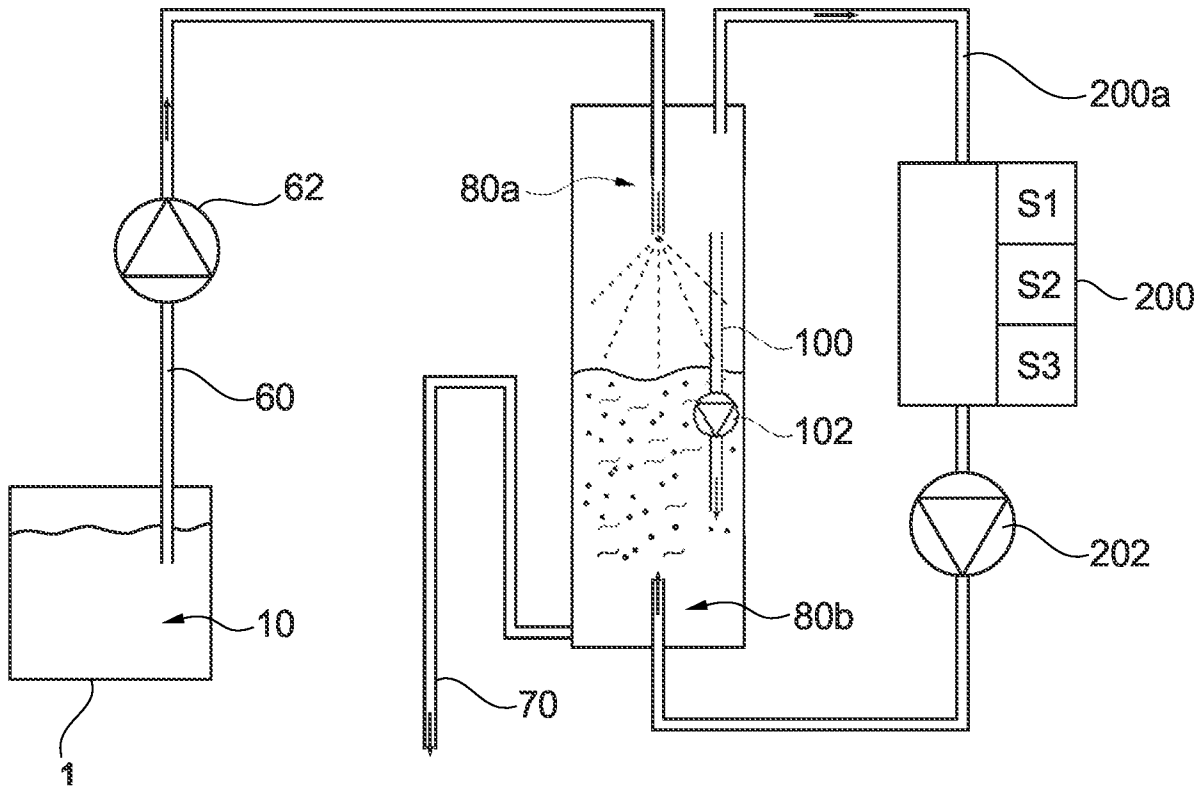


Fig. 2

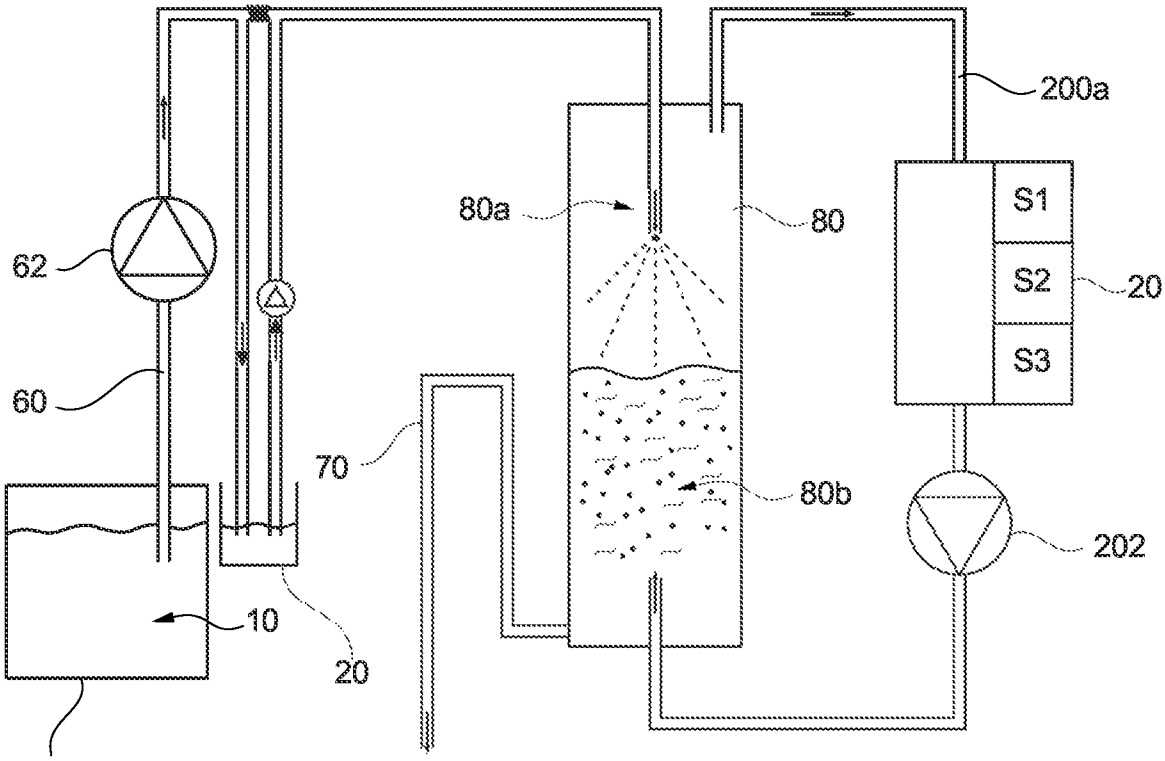


Fig. 3

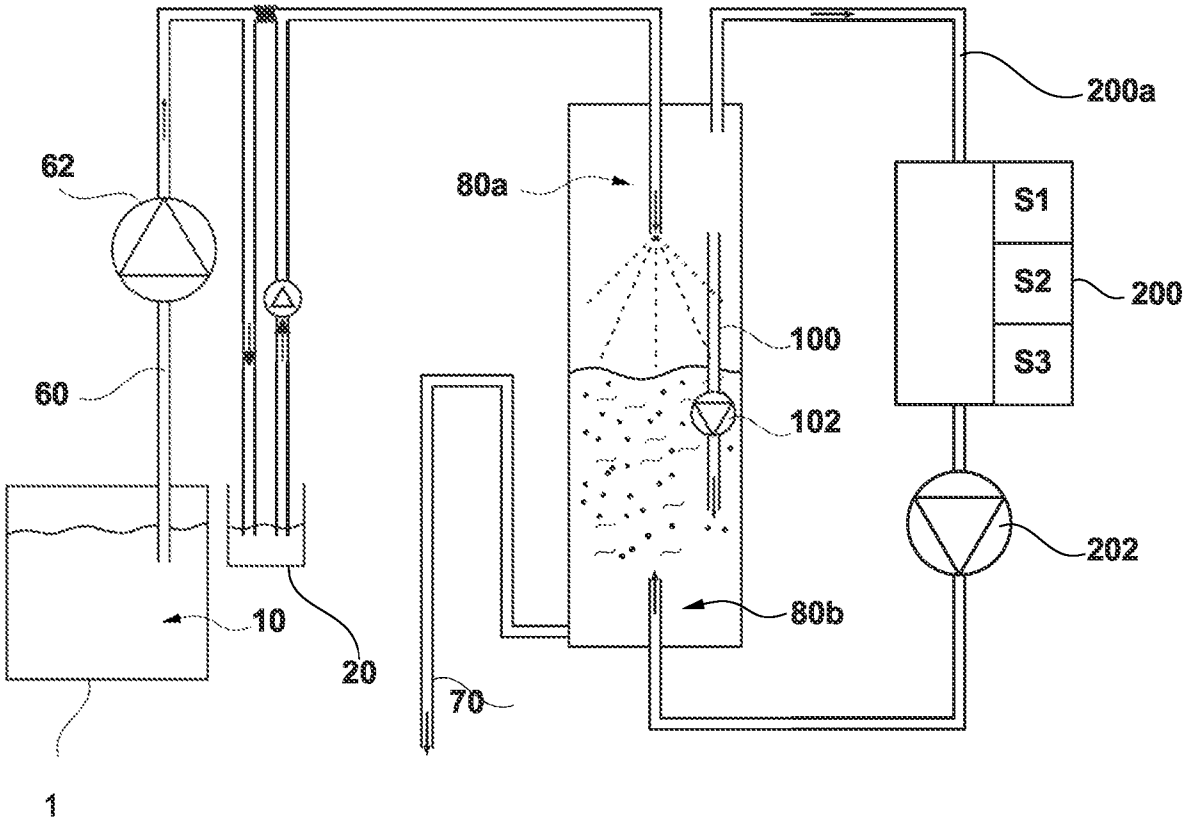


Fig. 4

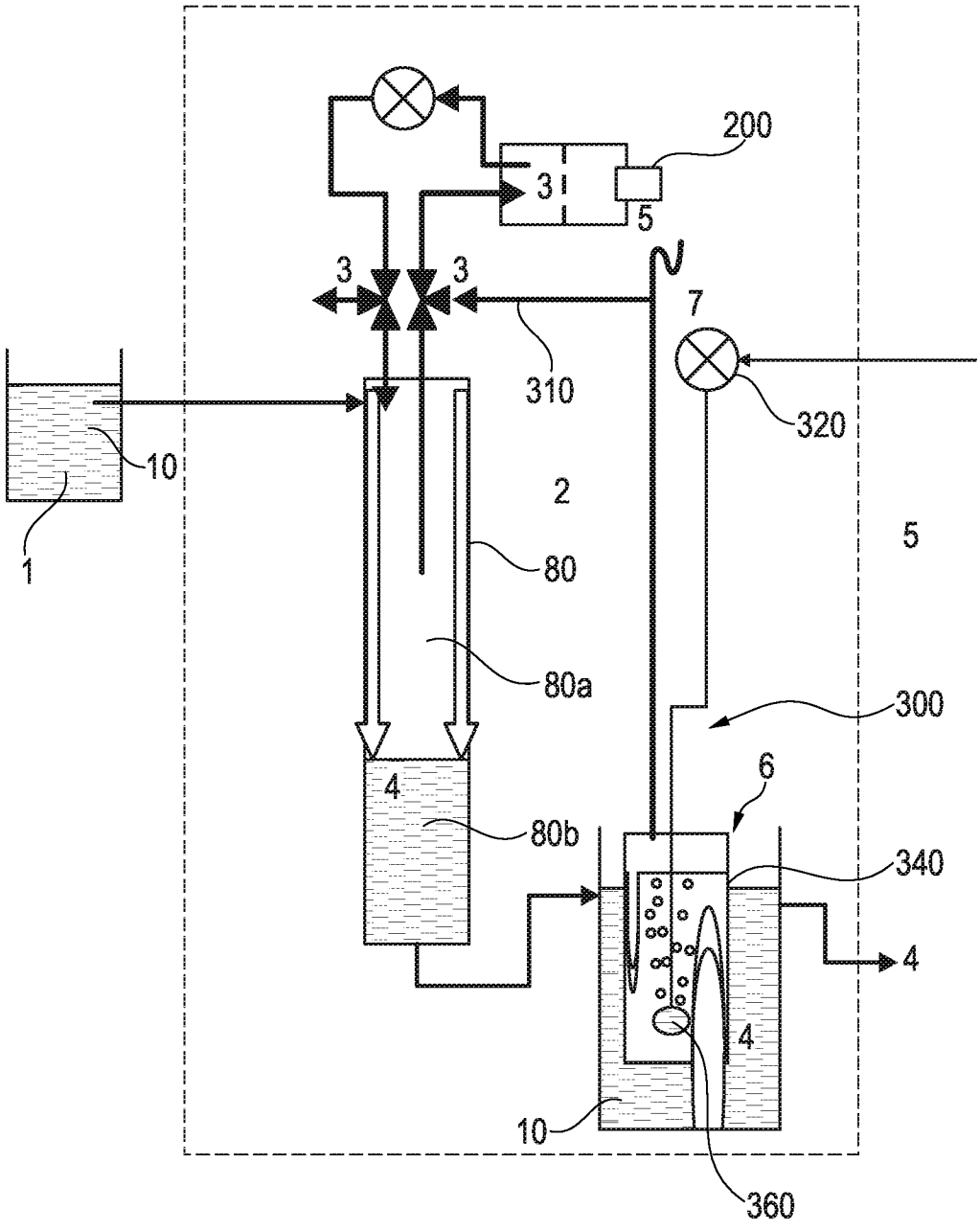


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2024/000003

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D, Y	NO 20210604 A1 (SEARAS AS), 14 November 2022 (2022-11-14); whole document --	1-52
Y	CN 113777262 A (UNIV TONGJI), 10 December 2021 (2021-12-10); figure 1; claims 1,3,9 --	1-52
A	EP 1697739 A1 (LAR ANALYTIK UND UMWELTMESSTEC ET AL), 6 September 2006 (2006-09-06); claims 1,11 --	1-52
A	CN 211348203 U (SECOND INST OF OCEANOGRAPHY MNR), 25 August 2020 (2020-08-25); abstract; figures 1-2; claim 1 --	1-52

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14-08-2024	14-08-2024

Name and mailing address of the ISA/SE	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2024/000003

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3756069 A (CARSWELL J ET AL), 4 September 1973 (1973-09-04); abstract; figures 1-2	1-52

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International application No.
PCT/NO2024/000003

Continuation of: second sheet

International Patent Classification (IPC)

G01N 33/18 (2006.01)

NO	20210604	A1	14/11/2022	NONE			
CN	113777262	A	10/12/2021	NONE			
EP	1697739	A1	06/09/2006	AT	E450793	T1	15/12/2009
				CN	1898562	A	17/01/2007
				DE	10360445	A1	28/07/2005
				DE	502004010467	D1	14/01/2010
				DE	202004000483	U1	01/04/2004
				RU	2006122996	A	27/01/2008
				RU	2347221	C2	20/02/2009
				US	20080026482	A1	31/01/2008
				US	7803631	B2	28/09/2010
				WO	2005064329	A1	14/07/2005
CN	211348203	U	25/08/2020	NONE			
US	3756069	A	04/09/1973	NONE			